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13. ABSTRACT (Maximum 200 words) The ground state of the cation, three lowest electronic states of the neutral, and two anionic states of Li <sub>3</sub> O were studied using different ab initio techniques. Stationary points on the potential energy surfaces were determined both at complete active space (CAS) self-consistent field (SCF) and at second-order Møller-Plesset (MP2) levels of theory. Excited states were approached using the single-excitation configuration interaction (CIS) method. Electron detachment energies for the anionic and neutral states were calculated at the quadratic configuration interaction (QCI) level with single, double, and approximate triple excitations (SD(T)) included. The calculations indicate that Li <sub>3</sub> O <sup>-</sup> possesses two bound electronic states. The ground <sup>1</sup> A <sub>1</sub> ' state has an equilibrium D <sub>3h</sub> structure and a vertical electron detachment energy (VDE) of 0.66 eV. The <sup>3</sup> E' bound state pseudorotates through <sup>3</sup> A <sub>1</sub> and <sup>3</sup> B <sub>2</sub> stationary points. The barrier for pseudorotation was found to be less than 0.002 eV at the QCISD(T) level. Two VDE peaks for the <sup>3</sup> E' anion were predicted to be at 0.45 and 1.15 eV, for transitions to the ground and the first excited state of the neutral, respectively. The ground state of the cation and the first three electronic states of the neutral Li <sub>3</sub> O were also considered and the vertical ionization potential for the ground neutral state was found to be 3.60 eV. Li <sub>3</sub> O and Li <sub>3</sub> O <sup>-</sup> are thermodynamically stable with respect to the unimolecular decompositions Li <sub>3</sub> O <sup>(-o)</sup> → Li <sub>2</sub> O + Li <sup>(-o)</sup> . Hence the species should be amenable to experimental studies.			
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by

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## Anionic and Neutral States of $\text{Li}_3\text{O}$

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### Abstract

The ground state of the cation, three lowest electronic states of the neutral, and two anionic states of  $\text{Li}_3\text{O}$  were studied using different ab initio techniques. Stationary points on the potential energy surfaces were determined both at complete active space (CAS) self-consistent field (SCF) and at second-order Møller-Plesset (MP2) levels of theory. Excited states were approached using the single-excitation configuration interaction (CIS) method. Electron detachment energies for the anionic and neutral states were calculated at the quadratic configuration interaction (QCI) level with single, double, and approximate triple excitations (SD(T)) included. The calculations indicate that  $\text{Li}_3\text{O}^-$  possesses two bound electronic states. The ground  $^1\text{A}_1'$  state has an equilibrium  $\text{D}_{3h}$  structure and a vertical electron detachment energy (VDE) of 0.66 eV. The  $^3\text{E}'$  bound state pseudorotates through  $^3\text{A}_1$  and  $^3\text{B}_2$  stationary points. The barrier for pseudorotation was found to be less than 0.002 eV at the QCISD(T) level. Two VDE peaks for the  $^3\text{E}'$  anion were predicted to be at 0.45 and 1.15 eV, for transitions to the ground and the first excited state of the neutral, respectively. The ground state of the cation and the first three electronic states of the neutral  $\text{Li}_3\text{O}$  were also considered and the vertical ionization potential for the ground neutral state was found to be 3.60 eV.  $\text{Li}_3\text{O}$  and  $\text{Li}_3\text{O}^-$  are thermodynamically stable with respect to the unimolecular decompositions  $\text{Li}_3\text{O}^{-(0)} \rightarrow \text{Li}_2\text{O} + \text{Li}^{-(0)}$ . Hence the species should be amenable to experimental studies.

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## I. Introduction

Recent theoretical studies indicate that neutral molecular radicals containing alkali metal atoms can accommodate more than one bound anionic state. The simple alkali metal oxide diatomic molecules possess electronically bound anionic states of  $^3\Pi$ ,  $^1\Pi$ ,  $^1\Sigma^+$ , and  $^3\Sigma^+$  symmetry [1]. Experimental [2,3] and theoretical [4] studies on alkali metal trimer anions ( $M_3^-$ ) have concentrated primarily on the lowest  $^1\Sigma_g^+$  isomer. Recently, we demonstrated that one triplet ( $^3A_2'$ ) and two quintet ( $^5A_1''$  and  $^5A_2'$ ) states of  $Li_3^-$  and  $Na_3^-$  are also electronically stable for a wide range of molecular geometries [5]. Also  $LiFLi^-$  possesses two electronically bound states of  $^1\Sigma_g^+$  and  $^3\Sigma_u^+$  symmetry [6].

The neutral  $Li_3O$  has already been studied both experimentally [7] and theoretically [8-11]. Wu et al. identified  $Li_3O$  in the course of their study on the nature of gaseous species over solid lithium oxides [7]. The values of the ionization potential, atomization energy, and dissociation energy to produce  $Li + Li_2O$  were found to be  $4.54 \pm 0.2$  eV,  $228.7 \pm 2$  kcal/mol, and  $50.7 \pm 10$  kcal/mol, respectively [7,12].

$Li_3O$  is an example of a "hypermatalated" molecule with a stoichiometry which violates the octet rule [8]. In addition, it is a promising candidate for being a "superalkali", (i.e., a molecular system whose first ionization potential is smaller than that of the Cs atom [9-11]). Both of these unusual chemical features are related to the nature of the highest occupied molecular orbital (HOMO). It displays bonding interactions between pairs of Li "ligands" which help to offset the octet-rule-violating structure and antibonding Li-O interactions.

Early predictions of a  $C_{2v}$  equilibrium structure for  $Li_3O$  [8] have not been confirmed in more advanced calculations [13,10] which indicated a  $D_{3h}$  structure, similar to that of  $Li_3O^+$ . Theoretical predictions of the adiabatic and vertical ionization potential produced 3.55 and 3.45 eV, respectively [10,11], far outside the range of experimental values [7], although the theoretical dissociation energy of 47.1 kcal/mol [10] agrees well with the experimental prediction.

To the best of our knowledge, neither the excited electronic states of the neutral nor the anionic states of  $\text{Li}_3\text{O}$  have yet been experimentally studied.

## II. Computational Aspects

For the lithium atom, we used the Dunning (9s5p/3s2p) one-electron basis set [14] supplemented with diffuse s and p functions with the same exponent 0.0074 [15] and one d function with the exponent 0.2 [16]. This basis set is detailed in Ref. [5]. For the oxygen atom we employed Dunning's aug-cc-pVDZ basis set which was designed to describe anionic species [17]. Cartesian d functions were used throughout the calculations and the full basis set for the molecule consists of 82 contracted gaussian functions.

Potential energy surfaces were explored within a complete active space (CAS) self-consistent field (SCF) formalism as well as at the second-order Møller-Plesset (MP2) theory level.

In CAS SCF calculations we imposed a constraint that molecular orbitals which result from the core 1s atomic orbitals were doubly occupied in every configuration state function (CSF). The neglected core-core and core-valence correlation effects are negligible for the lithium and oxygen atoms due to the low polarizability of the 1s cores. The remaining eight (cation), nine (neutral) or ten (anion) electrons were distributed in all possible ways among four  $a_1$ , two  $b_1$ , and two  $b_2$  molecular orbitals (the  $C_{2v}$  symmetry labeling is used). This choice of the active space led to 1764, 2352, 1176, and 1512 CSF's for the cation, neutral, singlet and triplet anion, respectively. The CAS SCF calculations were performed with the Utah MESS-KIT modular electronic structure codes [18] which generate analytical second geometrical derivatives. Stationary points on the potential energy surfaces were determined using our automated surface walking algorithm [19].

In the case of the neutral  $2^2A_1$  state, which correlates with the  $2E'$  state, the CAS SCF optimization was hindered by the problem of "root-flipping" [20]. Since the MP2 approach is inapplicable for excited electronic states, we invoked single-excitation configuration

interaction (CIS) approach [21] to determine geometry and relative energy of the  $2^2A_1$  transition state. The CIS results for the doublet neutral state should be considered cautiously. In the CIS approach, creation of spin eigenstates relies on having an RHF ground state and non-interaction of singlets and triplets does not carry over to doublets and quartets with a UHF reference. The Gaussian 92 code [22] attempts to handle these doublet cases but the theory is not clean anymore [23]. In view of the above doubts, we "calibrated" the CIS approach on the  $2^2B_2$  electronic state which also correlates with  $2^2E'$  but for which the CAS SCF and MP2 approaches are straightforwardly applicable.

In the MP2 geometry optimizations we allowed for the correlation of the core orbitals. In general, the structures corresponding to stationary points are quite similar at the CAS SCF and MP2 levels what suggests that the core-core and core-valence correlation effects are not important for geometrical predictions.

The restricted CAS SCF approach is capable to predict accurate geometries but it is inappropriate to accurately compare energies of species with a different number of electrons. Hence we employed the quadratic configuration interaction (QCI) approach with single, double and approximate triple excitations (SD(T)) [24] to determine relative energies and electron detachment energies. The QCISD(T) approach is size-extensive and takes into account dynamical correlation effects. In the QCI calculations, we kept the eight core electrons uncorrelated. We checked in our earlier study on  $LiFLi^-$  [6] that such a restriction changes the vertical detachment energy for the ground state anion by less than 0.003 eV. The QCI results were obtained with the Gaussian 92 suite of codes [22].

### III. Results

The stationary points on the potential energy surfaces of the cation, neutral, and anion determined at the CAS SCF and MP2 levels are characterized at Table 1 and the geometrical parameters used are defined in Fig. 1. The vibrational frequencies were calculated using analytical second derivatives. For the excited  $2^2B_2$  and  $2^2A_1$  states of

the neutral, stationary points are also reported at the CIS level. The spatial extents of the electronic charge distributions are characterized by the SCF values of  $\langle R^2 \rangle$ . The reported relative energies were obtained at the QCISD(T) level, as were our vertical (VDE) and adiabatic electron affinities ( $EA_a$ ) presented in Tables 2 and 3 for the neutral and the anion, respectively.

#### A. The Cation and Neutral

The  $D_{3h}$  electronic configuration for the closed-shell cation involves an orbital occupation  $3a_1'^2 2e' 21a_2''^2$  (the core  $1s$  orbitals are not included in this labelling) which will be denoted (+). Our  $D_{3h}$  geometry and frequencies for the closed-shell cation are quite similar at the CAS SCF and MP2 levels. They are also in a good agreement with the results of Rehm et al. [10]. The pyramidization mode ( $a_2''$ ), which lowers symmetry to  $C_{3v}$ , has the lowest frequency. Interestingly, the cation  $H_3O^+$ , studied earlier [25] has a  $C_{3v}$  equilibrium structure with the  $D_{3h}$  barrier of only 1.07 kcal/mol [26].

The MP2 equilibrium structure of the ground state neutral with the electronic configuration (+)  $4a_1'$  is again  $D_{3h}$  and similar to that of the cation. Because the  $^2A_1'$  wavefunction is found to have a single configuration character, the MP2 prediction should be quite accurate. Unexpectedly, the  $e'$  (in-plane) vibrational mode has an imaginary frequency at the CAS SCF level. Doubting whether the CAS SCF  $e'$  imaginary frequency is physically meaningful, we carried out a CAS SCF search for a new stationary point in  $C_{2v}$  symmetry and found a structure with  $R_1=1.683$  Å,  $R_2=1.731$  Å,  $\vartheta=133^\circ$  and an energy 0.06 eV lower than at the  $D_{3h}$  stationary point. However, the QCISD(T) energy is lower by 0.02 eV at the  $D_{3h}$  than at the  $C_{2v}$  CAS SCF stationary point. Hence, we conclude that the  $D_{3h}$  structure corresponds to a genuine minimum and the CAS SCF approach suffers for symmetry breaking artifacts [27]. Even though this  $^2A_1'$  state has a  $D_{3h}$  equilibrium structure, the MP2 vibrational frequencies of the  $a_2''$  and  $e'$  modes are much softer than in the underlying cation which implies that  $C_{3v}$ ,  $C_{2v}$ , and  $C_s$  symmetries are easily accessible by vibrational movement.

The  $4a_1'$  HOMO of the neutral is dominated by Li 2s orbitals which interact constructively with each other and destructively with small s-type contributions from the central O atom, as observed in Refs. [8-10]. The Mulliken-population atomic charges are +0.20 and -0.60 for Li and O, respectively. Our values for the VDE and  $EA_a$  of this ground state of  $Li_3O$  are 3.60 and 3.59 eV, respectively, in a good agreement with the electron propagator theory VDE of 3.45 eV [11]. However, these results disagree with the experimental estimation of  $4.54 \pm 0.2$  eV [7]. The theoretical VDE for  $Li_3O$  is lower than that of alkali metal atoms, so our result support the claimed "superalkali" nature of  $Li_3O$  [9-11].

The first excited state for the neutral of  $2E'$  symmetry has a dominant orbital occupancy of  $(+ )3e'$  and is subject to first-order Jahn-Teller (FOJT) distortion. Geometry optimization for the resulting  $2B_2$  component of this state is straightforward and the resulting CAS SCF and MP2 geometries and frequencies are quite similar. Due to problems with "root-flipping" at the CAS SCF level, geometry optimization for the  $2^2A_1$  component of this  $2E'$  state was performed at the CIS level. The reliability of the CIS approach was tested on the  $2B_2$  state where the stationary point characteristics were found to be similar for the CIS, CAS SCF, and MP2 approaches. We therefore believe that application of the CIS approach to the  $2^2A_1$  state is justified.

Pseudorotation in the  $2E'$  state is depicted in Fig. 2. Estimating the pseudorotation barrier requires a consistent calculation of the  $2^2A_1$  and  $2B_2$  energies. A QCISD(T) estimate for the  $2^2A_1$  energy was obtained using the following approximation:  $E_{QCI}(2B_2) - E_{CIS}(2B_2) + E_{CIS}(2^2A_1)$ , because only the CIS method could be applied directly to the  $2^2A_1$  state. The barrier for pseudorotation thus found was less than 0.04 eV.

The CIS oscillator strength for the  $2E' \leftarrow 2^2A_1'$  transition is 0.48 and the QCISD(T) vertical excitation energy is 0.728 eV. Interestingly, the neutral  $2E'$  state thus produced would be in the neighborhood of its conical intersection. This fact could be reflected in the dynamics of the  $2E'$  state, which might be studied using time dependent two-photon ionization techniques [28].



The next excited state of  $\text{Li}_3\text{O}$  has  $^2A_2''$  symmetry and  $(+)2a_2''$  orbital occupancy and an equilibrium  $D_{3h}$  structure. In comparison with the cation, the vibrational frequencies are quite similar and the equilibrium R is somewhat shorter. These features are consistent with the "out-of-the-plane" nature of the  $2a_2''$  orbital and similar trends were observed in the alkali metal trimers with the unpaired electron in an  $a_2''$  orbital [5,29]. In  $\text{Li}_3\text{O}$ , the  $2a_2''$  orbital is dominated by the Li 2p atomic orbitals with constructive Li-Li and destructive Li-O interactions. The CIS oscillator strength for the  $^2A_2'' \leftarrow ^2A_1'$  transition is 0.32 and the QCISD(T) vertical excitation energy is 1.551 eV.

## B. The Anion

The ground electronic state of  $\text{Li}_3\text{O}^-$  has a  $D_{3h}$  equilibrium structure with a geometry close to that of the cation and that of the ground state neutral. There is again a significant difference between the  $a_2''$  out-of-plane vibrational frequency calculated at the MP2 and CAS SCF levels, but this time both approaches predict a  $D_{3h}$  minimum. The MP2 frequencies are quite similar for the anion and the  $^2A_1'$  neutral.

The wavefunction for the anionic  $^1A_1'$  state is dominated by the  $(+)4a_1'^2$  configuration, but two equivalent contributions from the  $(+)3e'^2$  configuration are also important and have CI coefficients of 0.30 each. This feature is consistent with the low separation between the  $^2A_1'$  and  $^2E'$  states of the neutral (0.7 eV) and suggests that  $^3E'$  anionic state may be also electronically stable. The VDE for the  $^1A_1'$  anion state is 0.656 eV and the electron detachment peak is expected to be sharp because the anion and neutral equilibrium structures are very similar.

In addition to the ground  $^1A_1'$  state, the anion  $\text{Li}_3\text{O}^-$  possesses a second electronically bound state of  $^3E'$  symmetry with the dominant electronic configuration  $(+)4a_1'3e'$ . Due to FOJT distortion, stationary points develop on  $^3B_2$  and  $^3A_1$  surfaces. Both CAS SCF and MP2 approaches locate a transition state on the  $^3B_2$  surface with negative curvature along the  $b_2$  distortion mode. The surface must, however,

be extremely flat since at the QCISD(T) level the relative order of the  $^3B_2$  and  $^3A_1$  stationary points is changed, giving  $^3B_2$  lower than  $^3A_1$  by 0.001 eV, whereas the difference at the MP2 level was 0.011 eV with the opposite order. Clearly, the pseudorotation, as depicted on Fig. 2, is practically free and the numerical values of the  $b_2$  mode frequency are probably of little reliability.

The electron detachment energies for the pseudorotating  $^3E'$  state were calculated at both daughter-state stationary points (see Table 3). The detachment energies to the ground  $^2A_1'$  state of the neutral are predicted to lie in the range 0.43-0.46 eV. The detachment energies to the higher pseudorotating  $^2E'$  state of the neutral lie within 1.1-1.2 eV. We thus conclude that the electron detachment peaks from the  $^3E'$  anion state would bracket the anion's ground state detachment peak at 0.66 eV. Hence, the  $^3E'$  state may be amenable to experimental detection, providing a significant concentration of the triplet can be produced in the source.

Another feature which makes  $Li_3O$  and  $Li_3O^-$  suitable for experimental studies is their thermodynamic stability. The energy barrier (corrected for zero-point vibrations) for the decomposition  $Li_3O(+0^-) \rightarrow Li_2O + Li(+0^-)$  is predicted to be 84.40, 44.54, and 46.03 kcal/mol for the cation, neutral, and anion, respectively. The increased stability of the anion compared to that of the neutral reflects the fact that the electron affinity is larger for  $Li_3O$  than for  $Li$ . Our decomposition energy for the neutral is within the range of experimental data  $50.7 \pm 10$  kcal/mol [7,12].

#### IV. Conclusions

Theoretical calculations indicate that  $Li_3O^-$  can possess more than one bound electronic state. The fully symmetric singlet state is the ground state, but a triplet state is also electronically bound. Although only the anionic states of  $Li_3O^-$  were studied in this work, the preliminary results for the isoelectronic  $Li_4N^-$  produce a VDE from the  $^1A_1$  state of ca. 0.51 eV. For the  $^3T_2$  state of  $Li_4N^-$ , the VDE is ca. 0.17 eV, whereas detachment to the  $^2T_2$  state of the neutral  $Li_4N$  would require ca. 0.98 eV.

For the ground  $^1A_1'$  state of  $Li_3O^-$ , the electron detachment energy is 0.66 eV. The cation, ground state neutral, and the anion all have the equilibrium  $D_{3h}$  geometries, with the O-Li distances in the range 1.71-1.69 Å (MP2 level).

The pseudorotating anionic  $^3E'$  state is electronically stable with respect to the  $^2A_1'$  and  $^2E'$  states of the neutral by ca. 0.4 and 1.1 eV, respectively. The geometrical features of the daughter-state  $^3A_1$  and  $^3B_2$  stationary points are consistent with the bonding/antibonding interactions among the atomic orbitals contributing to the anion's singly occupied molecular orbitals. The QCISD(T) energies of the two stationary points are the same to within 0.002 eV. Hence, the pseudorotation is practically free.

For the neutral  $Li_3O$ , we studied the  $^2E'$  and  $^2A_2''$  excited states in addition to the  $^2A_1'$  ground state. The  $^2E'$  state pseudorotates through a  $^2B_2$  minimum and a  $^2A_1$  transition state with a pseudorotation barrier of ca 0.04 eV. The oscillator strength for the  $^2E' \leftarrow ^2A_1'$  transition is 0.48 and the corresponding vertical excitation energy is 0.728 eV.

The  $^2A_2''$  neutral, with a  $D_{3h}$  equilibrium structure, is separated from the ground state neutral by 1.551 eV, and is easily accessible since the oscillator strength is 0.32.

Our vertical and adiabatic ionization potentials for  $Li_3O$  of 3.60 and 3.59 eV, respectively, disagree with the experimental value of  $4.54 \pm 0.2$  eV [7], yet agree with other theoretical predictions [10,11].

All of the species discussed in this study are thermodynamically stable with respect to unimolecular decomposition. Hence, the neutral and the anion are more amenable to experimental studies than their hydrogen-substituted analogs  $H_3O$  and  $H_3O^-$ , which are thermodynamically unstable [25].

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### Captions for Figures

Figure 1. Geometrical parameters for the  $C_{2v}$  structure of the  $Li_3O$  neutral and anionic species.

Figure 2. Graph representing the pseudorotation for anionic or neutral  $Li_3O$ .

Table 1. Stationary points (distances R in Å,  $\phi$  in degrees) and harmonic frequencies ( $\text{cm}^{-1}$ ) for different electronic states of the cation, neutral, and anion of  $\text{Li}_3\text{O}$ . The spatial extent of the SCF electronic charge distribution  $\langle R^2 \rangle$  is given in a.u., and the relative energies (QCISD(T) level) are in eV. The dominant electronic configurations (DEC) are given with respect to the closed-shell cationic core  $3a_1'^2 2e'^2 1a_2'^2$ , which is denoted (+).

Species	Symmetry	State	DEC	Method	Geometry	Vibrational Frequencies <sup>a</sup>	$\langle R^2 \rangle$	EqQ
$\text{Li}_3\text{O}^+$	$D_{3h}$	$1A_1'$	(+)	CAS	R=1.726	$a_2''$ 244, $e'$ 265, $a_1'$ 655, $e'$ 806	91	0.0
				MP2	R=1.708	$e'$ 270 (73), $a_2''$ 291 (270), $a_1'$ 687 (0), $e'$ 853 (290)		
$\text{Li}_3\text{O}$	$D_{3h}$	$2A_1'$	(+) $4a_1'$	CAS	R=1.707	$e'$ 251i, $a_2''$ 77, $a_1'$ 669, $e'$ 767	141	-3.593
				MP2	R=1.694	$e'$ 135 (462), $a_2''$ 180 (2), $a_1'$ 699 (0), $e'$ 869 (109)		
$\text{Li}_3\text{O}$	$C_{2v}$	$2B_2$	(+) $3b_2$	CAS	R1=1.705 R2=1.707 $\phi=114.58$	$b_1$ 193, $b_2$ 215, $a_1$ 219, $a_1$ 679, $a_1$ 801, $b_2$ 871	153	-2.890
				MP2	R1=1.690 R2=1.707 $\phi=114.96$	$b_2$ 202 (9250), $a_1$ 213 (87), $b_1$ 243 (1), $a_1$ 687 (52), $b_2$ 844 (148), $a_1$ 849 (16)		
				CIS	R1=1.662 R2=1.699 $\phi=117.96$	$b_1$ 210, $b_2$ 229, $a_1$ 244, $a_1$ 697, $b_2$ 814, $a_1$ 903		
$\text{Li}_3\text{O}$	$C_{2v}$	$2^2A_1$	(+) $7a_1$	CIS	R1=1.718 R2=1.671 $\phi=121.08$	$b_2$ 132i, $b_1$ 211, $a_1$ 424, $a_1$ 702, $b_2$ 745, $a_1$ 1025		-2.854b)

Table 1. (continued)

Species	Symmetry	State	DEC	Method	Geometry	Vibrational Frequencies <sup>a)</sup>	$\langle R^2 \rangle$	EqQ
Li <sub>3</sub> O	D <sub>3h</sub>	2A <sub>2</sub> <sup>''</sup>	(+)2a <sub>2</sub> <sup>''</sup>	CAS	R=1.706	a <sub>2</sub> <sup>''</sup> 215, e' 232, a <sub>1</sub> ' 678, e' 804	189	-2.042
				MP2	R=1.697	e' 232 (403), a <sub>2</sub> <sup>''</sup> 247 (4), a <sub>1</sub> ' 702 (0), e' 839 (1353)		
Li <sub>3</sub> O <sup>-</sup>	D <sub>3h</sub>	1A <sub>1</sub> '	(+)4a <sub>1</sub> ' <sup>2</sup>	CAS	R=1.708	a <sub>2</sub> <sup>''</sup> 85, e' 180, a <sub>1</sub> ' 666, e' 748	274	-4.248
				MP2	R=1.697	e' 171 (77), a <sub>2</sub> <sup>''</sup> 172 (179), a <sub>1</sub> ' 693 (0), e' 856 (214)		
Li <sub>3</sub> O <sup>-</sup>	C <sub>2v</sub>	3A <sub>1</sub>	(+)6a <sub>1</sub> 7a <sub>1</sub>	CAS	R <sub>1</sub> =1.709 R <sub>2</sub> =1.707 ϕ=131.18	b <sub>2</sub> 144, b <sub>1</sub> 149, a <sub>1</sub> 257, a <sub>1</sub> 673, b <sub>2</sub> 723, a <sub>1</sub> 858	249	-4.023
				MP2	R <sub>1</sub> =1.717 R <sub>2</sub> =1.697 ϕ=129.23	b <sub>2</sub> 101 (123), b <sub>1</sub> 202 (166), a <sub>1</sub> 235 (316), a <sub>1</sub> 682 (5), b <sub>2</sub> 806 (781), a <sub>1</sub> 875 (458)		
Li <sub>3</sub> O <sup>-</sup>	C <sub>2v</sub>	3B <sub>2</sub>	(+)6a <sub>1</sub> 3b <sub>2</sub>	CAS	R <sub>1</sub> =1.700 R <sub>2</sub> =1.707 ϕ=109.43	b <sub>2</sub> 270i, b <sub>1</sub> 144, a <sub>1</sub> 191, a <sub>1</sub> 673, a <sub>1</sub> 761, b <sub>2</sub> 809	246	-4.024
				MP2	R <sub>1</sub> =1.692 R <sub>2</sub> =1.709 ϕ=109.81	b <sub>2</sub> 154i (6108), a <sub>1</sub> 176 (342), b <sub>1</sub> 200 (162), a <sub>1</sub> 682 (139), a <sub>1</sub> 824 (439), b <sub>2</sub> 845 (318)		

a) IR intensities (km/mol) in parenthesis

b) the energy of 2<sup>2</sup>A<sub>1</sub> is estimated as: EQCI(2B<sub>2</sub>) + ECIS(2<sup>2</sup>A<sub>1</sub>) - ECIS(2B<sub>2</sub>)



Table 2. Electron vertical detachment energies (VDE) and adiabatic electron affinities (EA<sub>a</sub>) (in eV) calculated at the QCISD(T) level for the transitions  $\text{Li}_3\text{O}^+ + e \leftarrow \text{Li}_3\text{O}$ .

Transition	VDE	EA <sub>a</sub>
$^1\text{A}_1' + e \leftarrow ^2\text{A}_1'$	3.603	3.593
$^1\text{A}_1 + e \leftarrow ^2\text{B}_2$	2.933	2.890
$^1\text{A}_1 + e \leftarrow ^2^2\text{A}_1^{\text{a)}$	2.954	2.909
$^1\text{A}_1' + e \leftarrow ^2\text{A}_2''$	2.052	2.042

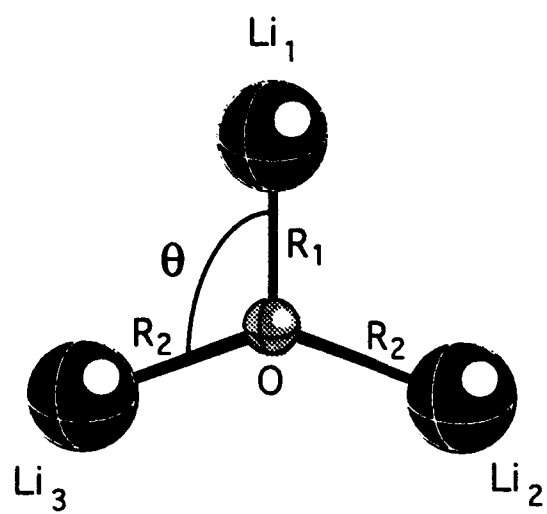
a) the energy of  $^2^2\text{A}_1$  is estimated as in Table 1

Table 3. Electron vertical detachment energies (VDE) and adiabatic electron affinities ( $EA_a$ ) (in eV) calculated at the QCISD(T) level for the transitions  $Li_3O + e \leftarrow Li_3O^-$ .

Transition	VDE	$EA_a$
$2A_1' + e \leftarrow 1A_1'$	0.656	0.656
$1^2A_1 + e \leftarrow 3A_1$	0.450	0.430
$2^2A_1 + e \leftarrow 3A_1$	1.346 <sup>a)</sup>	1.074 <sup>b)</sup>
$1^2A_1 + e \leftarrow 3B_2$	0.459	0.431
$2B_2 + e \leftarrow 3B_2$	1.151	1.134

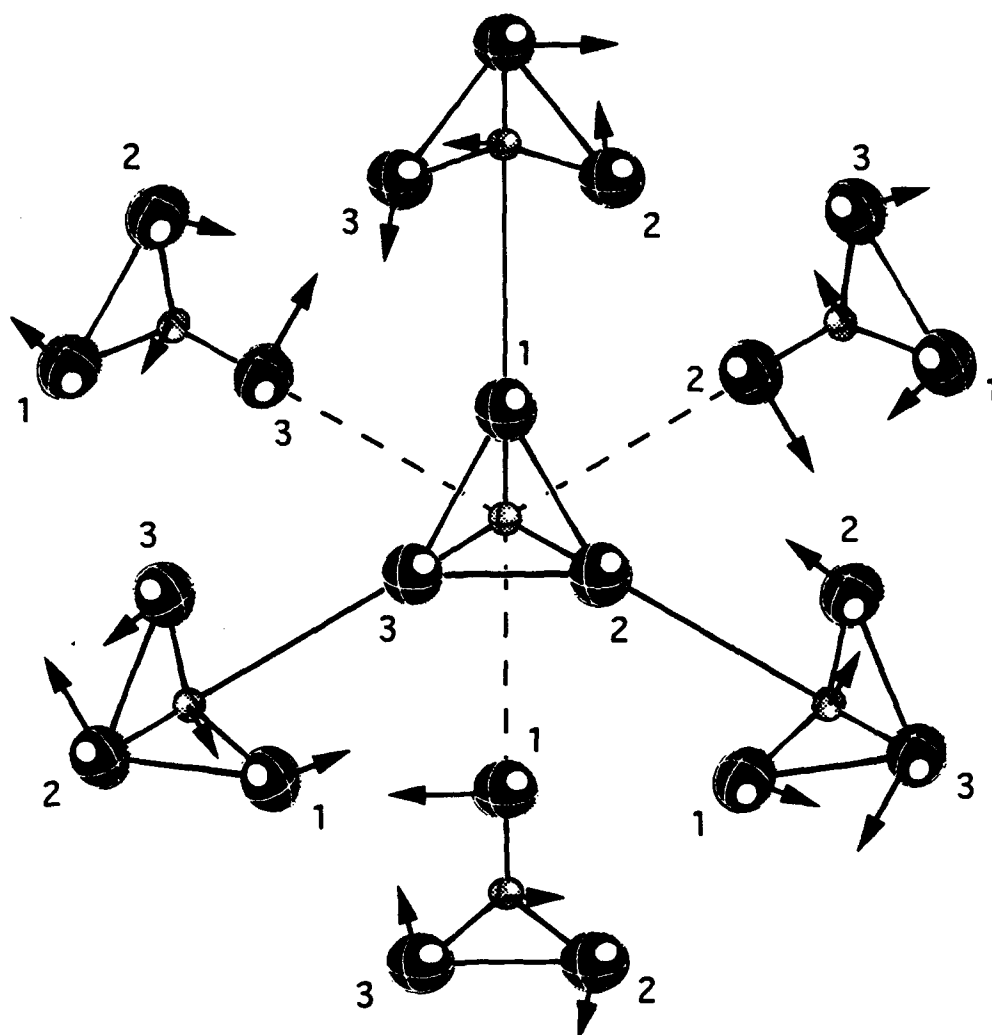
a) the VDE is estimated as:  $E_{QCI}(^3A_1) - E_{QCI}(^2B_2) + E_{CIS}(^2B_2) - E_{CIS}(2^2A_1)$ .

b) the  $EA_a$  is estimated as:  $VDE + E_{CIS}(2^2A_1 \text{ at the } ^3A_1 \text{ geometry}) - E_{CIS}(2^2A_1 \text{ at its CIS stationary point})$ .



Anionic and Neutral States of  
 $\text{Li}_3\text{O}$   
Gutowski, Simons

FIG. 1



# Anionic and Neutral States of $\text{Li}_3\text{O}$

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**FIG. 2**